

# Mechanochemical synthesis of vanadium nitride

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## Abstract

Vanadium nitride (VN) has been prepared by mechanosynthesis from vanadium metal under a pressurized nitrogen atmosphere in a short milling time. The characterization of the final product by X-ray diffraction, scanning electron microscopy, electron energy loss (EELS), and X-ray absorption spectroscopy (XAS) is presented. The final product, VN with 96% of purity, is obtained at room temperature with nanometric particle size and a very high microhardness after sintering. A relationship between microstructure and microhardness as well as a comparison between the VN obtained mechanical and thermal method is also presented.

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**Keywords:** Mechanosynthesis; Vanadium nitride; EELS; XAS; Microhardness

## 1. Introduction

Transition metal nitrides have attracted much attention in the last few years due to their special properties. In particular, vanadium nitride (VN) has extreme hardness, high-temperature stability, high thermal and electrical conductivity and corrosion resistance that make it a suitable compound for many uses. Traditional applications, of these materials range from cutting tools and structural materials,<sup>1,2</sup> to magnetic and electric components,<sup>3</sup> superconducting devices<sup>4–6</sup> and electrode material for super-capacitors.<sup>7</sup> Moreover there is increasing interest on, VN as an important industrial catalyst known for its selectivity and stability in hydroprocessing<sup>8–11</sup> and hydrotreating.<sup>12,13</sup> Also VN is a superconductor with transition temperature ranging from 2 to 9 K.<sup>8</sup>

Conventionally, vanadium nitride is prepared by direct nitridation of pure metal or by carbothermal reduction of an oxide, both processes under nitrogen or ammonia atmosphere at temperatures above 1000 °C.<sup>14–17</sup> Among the methods employed recently to synthesize VN there are: reactive magnetron sputter deposition,<sup>18</sup> rapid thermal processing,<sup>19</sup> ammonolysis of precursor compounds of metal,<sup>20,21</sup> thermal reduction–nitridation in an autoclave,<sup>22,23</sup> solid state

metathesis<sup>24</sup> and self-propagating high temperature synthesis<sup>25</sup>. The low temperature methods for the preparation of compounds are important to obtain a pure phase, strain free, fine particle with controlled morphology. In this way the synthesis by thermal liquid–solid reaction has reported good results.<sup>26</sup> On the other hand, mechanical alloying is considered as a method to synthesize particulate materials at room temperature such as amorphous phases, supersaturated solid solutions, metastable phases, intermetallic compounds, composites and ceramic materials.<sup>27–30</sup> Metal nitride phases have been obtained by ball milling of elemental powders in nitrogen or in dry ammonia atmospheres.<sup>30–35</sup> Vanadium nitride has been obtained from mechanical treatment by Calka and Williams,<sup>34</sup> using a planetary-type ball mill under nitrogen atmosphere with a milling time of 60 h. In the present study, we have synthesized vanadium nitride by mechanical treatment of metallic vanadium under pressure of nitrogen gas, in a planetary mill with a milling time of 8 h. The characterization of the final product and the comparison with that obtained from a thermal procedure is also included.

## 2. Experimental

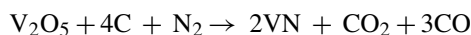
### 2.1. Synthesis

Vanadium powder (Aldrich, 99.5%) was milled under pressure of 11 bars of high purity nitrogen gas (H<sub>2</sub>O and O<sub>2</sub> < 3 ppm) using a modified planetary ball mill (Fritsch, model Pulverisette

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7). A steel vial of 45 cm<sup>3</sup> was used, with 6 steel balls and 5 g of V powder. The diameter and the weight of balls were 15 mm and 13.85 g, respectively, so the powder-to-ball mass ratio was 1:16. The vial was purged with nitrogen gas for several times, and afterwards the desired nitrogen pressure was selected prior to milling. The vial and the gas cylinder were connected through a rotary valve and a flexible polyamide tube, which allows working pressures up to 27 bars. The rotary valve can operate up to 25,000 rpm under pressures ranging from vacuum to 70 bars. In this way, the vial is permanently connected to the gas cylinder that supplies the gas at the desired pressure over the whole process. A spinning rate of 700 rpm for both the rotation of the supporting disc and the superimposed rotation of the vial in the opposite direction was always used.

Synthesis of vanadium nitride by carbothermal reduction of V<sub>2</sub>O<sub>5</sub>. The carbothermal reduction takes place according to the following overall reaction:



Vanadium pentoxide, V<sub>2</sub>O<sub>5</sub> (Panreac, 99%), was used as precursor with activated carbon (Aldrich 27,810-6). The nitrogen gas is introduced in the system by means of a mass-flow controller (UCAR) in such a way that the accurate flow control is insensitive to temperature disturbances.

The sample controlled reaction temperature (SCRT) equipment consisted of a high-temperature tubular furnace (carbolite 1600 °C) and a CO infrared sensor interfaced to a furnace temperature controller CO IR model SB-300, ADC) ranging from 0% to 2% of CO. The following gas in such an apparatus sweeps the CO generated in the reaction through an infrared detector, and the temperature of the sample is controlled in such a way that the CO concentration is maintained constant at a value previously selected by the user. Moreover, one can choose the constant reaction rate *C* at any particular concentration of CO by properly selecting the flow rate of the reactive gas and the weight of the sample.

## 2.2. Characterization

X-ray powder diffraction patterns were collected with a Siemens D501 instrument equipped with a scintillation counter using Cu K<sub>α</sub> radiation and a primary graphite monochromator; the scanning rate of the goniometer was 0.4° min<sup>-1</sup>. The full widths at half-maximum (FWHM) of (1 1 1) and (2 0 0) diffraction peaks of V and VN, respectively, were used to calculate the average diameter of the coherently diffraction domain with the Scherrer method.<sup>36</sup> The lattice parameter refinement corresponding to the final product was also calculated from the whole set of peaks of XRD diagram using the Lapods computer program<sup>37</sup> and assuming a cubic symmetry for VN.

Thermogravimetric (TG) diagrams for the different vanadium ground samples were recorded at a heating rate of 5 K/min, from room temperature to 1400 °C, using a nitrogen flow of 100 cm<sup>3</sup>/min, at a pressure of 1 bar. The conversion of V into VN during the milling process was calculated from the mass gains, assuming a stoichiometric nitride as the final product. The

validity of this indirect method was checked against an unground sample.

The iron contamination of the milling samples was calculated by Fe<sup>2+</sup> permanganometry.

The composition analysis was performed in a high resolution transmission electron microscope (Philips CM200, Eindhoven) with a super twin objective lens, working at 200 kV with a LaB<sub>6</sub> filament. The instrument is equipped with a parallel electron energy loss (EELS) spectrometer (Model 766-2K, Gatan, München, Germany). For observation, the sample was embedded in a resin, then a film of 100 nm was cut, which was supported on a holey carbon grid. The N and V core-loss edges were recorded in the diffraction mode with a camera length of 470 mm using a 2-mm spectrometer. Entrance aperture yielded an energy resolution at the zero-loss peak of 1.4 eV. Spectra were recorded for dark current and channel-to-channel gain variation. Commercial VN powders were measured in the same conditions as reference compounds. After subtraction of the background by a standard power-law function, the spectra were deconvoluted for plural scattering with the Fourier-ratio method and normalized to the jump. All of these treatments were performed within the EL/P program (Gatan).

XAS spectra at the V–K edge *E* = 5465 eV of the samples submitted to 0.5, 1.5, and 8 h milling times were recorded at the synchrotron radiation source ESRF in Grenoble, France, at station BM29. The ring energy was 6 GeV and the maximum stored current was 200 mA. A double crystal Si (3 1 1) monochromator was used. Higher harmonic rejection was carried out by detuning both crystals to 50% of the intensity of the first harmonic. Measurements were carried out at room temperature in transmission detection mode, using 45 cm ionization chambers as detectors, filled with the appropriate gas mixtures. The amount of sample used was that calculated to attain the optimum absorption  $\mu x = 2.5$ . Since the required amount of sample was rather small (a few milligrams), they were mixed with BN to reach the minimum size to build a self-supporting pellet.

Microstructural observations were conducted by using scanning electron microscopy (SEM model JSM 5400 Jeol). Photographs were recorded at 30 kV. The samples powder were dispersed in ethanol and supported on a metallic grid.

The specific surface area determination was performed using a single-point Brunauer–Emmett–Teller (BET) method with an adsorptometer (FlowSorb III 2310, Micromeritics Instruments).

Vickers microhardness measurements (FM-700, Future-Tech, Hardness tester) were conducted on the pellet cross-sections under a load of 1 kgf for 15 s. An average hardness was calculated from 20 indents per specimen.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the vanadium samples milled for various times at a pressure of 11 bars. Diagrams of the unground V and the commercial VN samples are presented as references. The analysis of the XRD patterns reveals a broadening of the V peaks increasing with milling time due to the refinement of the crystallite size, the formation of defects, and microstrains of the milled samples from 0.5 to 1.5 h. At the

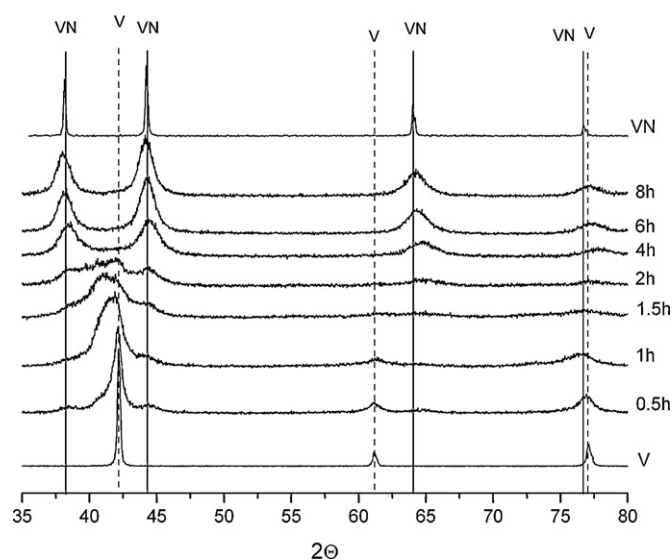


Fig. 1. X-ray diffraction patterns of vanadium ground from 0 to 8 h and the commercial VN for comparison.

same time, the diagrams begin to show peaks corresponding to vanadium nitride. After 2 h of milling VN peaks are the most important of the diagram. Further milling up to 8 h led to a continuous increase in the intensities of the VN diffraction peaks; the considerable broadening of the VN XRD peaks suggests that this phase was obtained with a very refined microstructure and a high microstrains content. The crystallite size of the different samples was estimated using the Scherrer equation, and the values have been included in Table 1. The dimension of the VN cubic unit cell and remaining V metal was determined from the whole set of peaks of the XRD diagram, recorded for  $2\theta$  values ranging from 10 to 90, for all samples. A least squares fitting of the XRD peaks were carried out with the Lapoud program.<sup>37</sup> A lattice parameter value of 4.1085 Å was obtained for the length of the axis “a” of the unit cell of the final product (powder milled for 8 h), this value is lower than that of the stoichiometric compound (4.1392 Å) and suggest that a nonstoichiometric VN<sub>x</sub> compound was obtained; studies for several transition metals of composition MN<sub>x</sub><sup>38–40</sup> have reported that the “a” parameter is very sensitive to the nitridation level.

Iron contamination was not clearly observed in the XRD patterns because the width of V and VN peaks can hide iron

peaks. The chemical analysis of the total iron content by titration showed that contamination by this metal took place during the grinding, although it never exceeded 9%, the corresponding percentage of iron and the surface area of the samples are included in Table 1.

In order to analyze whether the reaction was completed after milling, we have used an indirect method of analysis, thermogravimetry analysis. TG diagrams for the different vanadium ground samples were recorded at a heating rate of 5 K/min, from room temperature to 1400 °C, using a nitrogen flow rate of 100 cm<sup>3</sup>/min, at a pressure of 1 bar. Once 1400 °C was reached, the temperature was held until the maximum uptake of nitrogen was achieved. The conversion of V into VN during the milling process was calculated from the mass gain, assuming a stoichiometric nitride as the final product. The calculated nitrogen contents of the samples are shown in Table 2.

The composition of the samples was also calculated from the lattice parameter using the Vegard law for the solution solid between vanadium metal and nitrogen; the results obtained are shown in Table 2. Samples ground for 6 and 8 h show similar results.

On the other hand, the content of nitrogen in VN has also been calculated from the microscopy analysis, EELS. The EELS technique in transmission electron microscopy is very appropriate for the characterization of nanostructured samples, by recording core-level absorption edges at a microscopic level. Fig. 2(a–d) shows the N–K and V–L<sub>2–3</sub> edges for the ground samples prepared in the present work, and for the commercial VN for comparison purposes, recorded in different areas. The samples ground for 0.5–1.5 h (Fig. 2(a–c)), show spectra with nitrogen and vanadium peaks and others with only peaks of vanadium. Samples ground from 2 to 8 h show N–K edges peaks in all the samples, exhibiting the same shape, and thereby showing that the samples have the same structure (Fig. 2(d)). At the microscopic level, the samples ground for 4, 6 and 8 h are homogeneous, showing zones with similar atomic ratios of the elements. The composition of the material can be determined by integrating the number of counts under the peaks, and using relevant cross-sections provided by the Gatan EL/P software. Representative results from the quantitative analysis performed from Fig. 2d are shown in Table 2. The results are in good agreement with those obtained from XRD and TG for the samples ground for 6 and 8 h when the conversion of vanadium into vanadium nitride has been

Table 1  
Characterization of samples of vanadium ground from 0 to 8 h.

Grinding time	D (nm)		Microstrains $\langle \epsilon \rangle \times 10^{-3}$	Lattice parameter (Å)	%Fe (ca)	S <sub>BET</sub> (m <sup>2</sup> /g)
	V	VN				
0h	40	–	0.176	V-a=3.0274	0	1.5
0.5h	9.2	–	0.890	V-a=3.0347	5.2	0.4
1h	10.0	–	1.545	V-a=3.0347	7.2	0.6
1.5h	4.1	–	–	V-a=3.0535	6.1	1.5
2h	–	5.9	–	–	6.8	2.3
4h	–	5.1	1.192	VN-a=4.0787	6.5	2.6
6h	–	6.4	1.376	VN-a=4.0996	8.2	3.1
8h	–	5.5	1.143	VN-a=4.1085	8.9	3.1

Table 2  
Composition of samples of vanadium ground and EXAFS characterization.

Grinding time	Composition TG	Composition Vegard	Composition EELS	$a$ (Å) EXAFS		% EXAFS	
				V	VN	V	VN
0.5 h	VN <sub>0.1</sub>	–	–	3.02	4.02	90	10
1 h	VN <sub>0.1</sub>	–	VN <sub>0.38</sub>	–	–	–	–
1.5 h	VN <sub>0.19</sub>	–	VN <sub>1.01</sub>	3.06	4.04	84	16
2 h	VN <sub>0.39</sub>	–	VN <sub>0.96</sub>	–	–	–	–
4 h	VN <sub>0.65</sub>	VN <sub>0.82</sub>	VN <sub>1.00</sub>	–	–	–	–
6 h	VN <sub>0.84</sub>	VN <sub>0.89</sub>	VN <sub>1.12</sub>	–	–	–	–
8 h	VN <sub>0.96</sub>	VN <sub>0.93</sub>	VN <sub>1.14</sub>	3.80	4.12	10	90

almost completed. Discrepancies among the different techniques might be understood if a percentage of the sample has been amorphized. This team is possible because the mechanosynthesis method employed, induces a high degree of amorphization.

In this way, XAS techniques were also used for the characterization of the vanadium nitride. Three samples have been analyzed, 0.5, 1.5 and 8 h of grinding time. The normalized XANES spectra of the V–K absorption edge appearing at 5465 eV for these samples have been included in Fig. 3. The V–K edge is rather sensitive to the coordination environment and the oxidation state of the V compounds. For this reason, its overall shape has been used as a fingerprint by comparing it with that of other crystalline compounds of known structure.<sup>41</sup> The

XANES spectrum, of sample V 0.5 h, resemble that of the vanadium metal, while that of sample V 8 h of milling is similar to the spectrum of the VN compound, as can be deduced from the comparison with the corresponding spectra included in the inset, taken from Ref.<sup>42</sup> In the V 1.5 h sample spectrum, there seems to be an intermediate situation between the two previous XANES spectra. While maintaining the higher energy shoulder of the V 0.5 h spectrum, there is a hint of another shoulder at lower energies similar to that appearing in the V 8 h spectrum. Besides, the absorption edge energy is between the previous ones, as expected for a system with an intermediate mean oxidation state. The intensity of the EXAFS oscillations of the three spectra is rather low, particularly those of V 0.5 h and V 1.5 h samples;

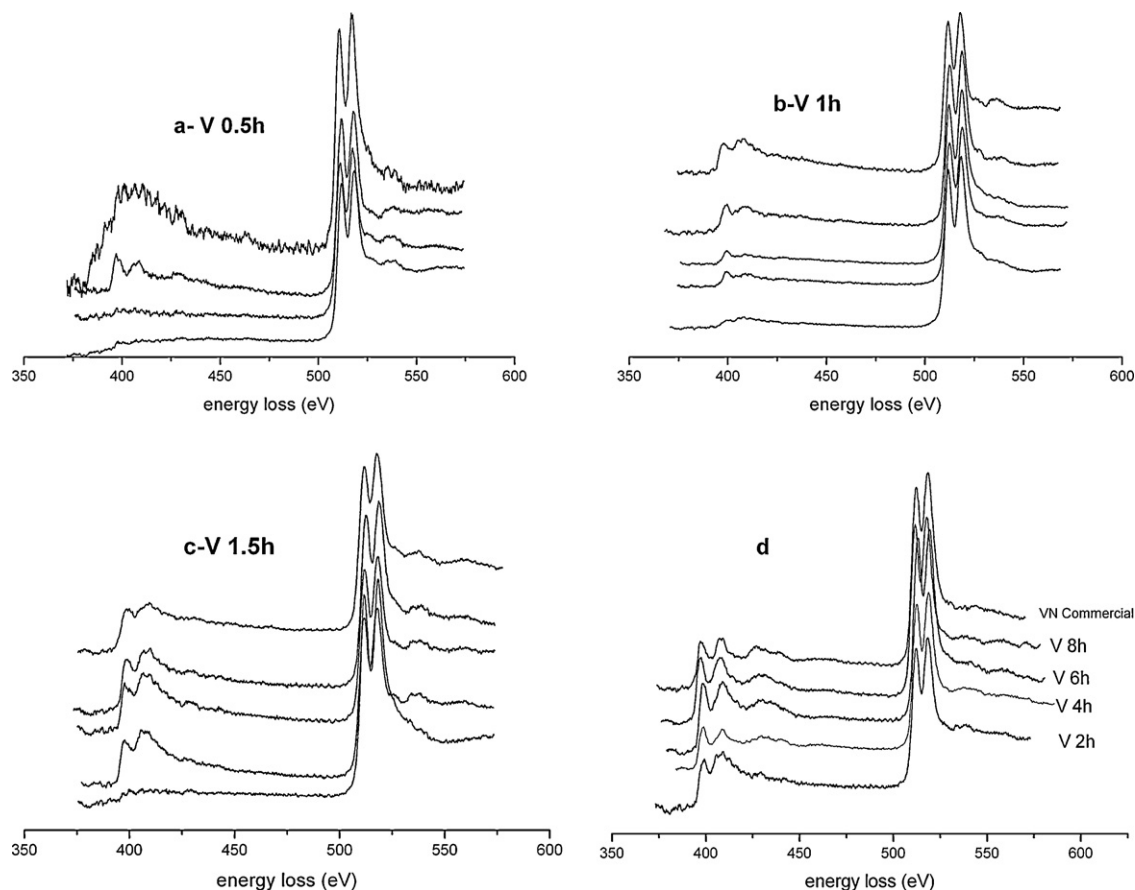


Fig. 2. Electron energy loss spectra N–K, V<sub>2,3</sub> corresponding to the ground samples of vanadium, (a) 0.5 h, (b) 1 h, (c) 1.5 h and (d) 2 h, 4 h, 6 h, 8 h and VN commercial.

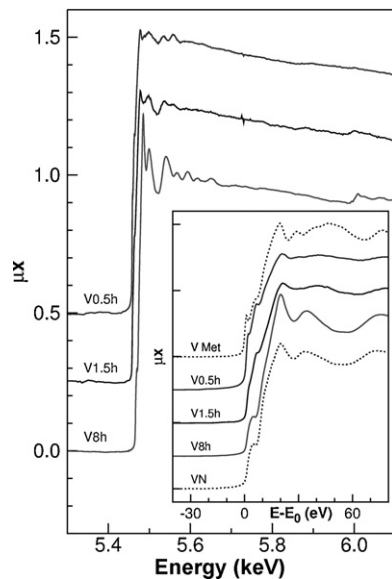


Fig. 3. XAS spectra V 0.5 h, V 1.5 h and V 8 h samples and insight the XANES region, including V metal and VN spectra for comparison.

this low intensity indicates that these samples should show a high degree of amorphization. The fits of the EXAFS spectra were performed by us in a previous work,<sup>43</sup> and a summary of the results is included in Table 2. We can see that the results obtained are in good agreement with others shown in Table 2. So, we can explain that the milling treatment distorts significantly the V–metal structure, reducing the particle size, increasing the number of defects, and expanding the V–bcc metal lattice. Thus, the sample becomes highly reactive against N<sub>2</sub>. The introduction of nitrogen atoms in the V–bcc structure expands the lattice to accommodate them, further expands getting more N atoms in it, becoming more similar to the VN structure. On the other hand, when VN is formed, the lattice parameter “a” increases with milling time as consequence of the N<sub>2</sub> introduction. The XRD patterns can be explained with this supposition, because at the same time that the V peaks gets down, VN peaks appear and rise. The grain size decreases when the milling time increases. According to this, the S<sub>BET</sub> increases, at the same time that the milling time increases.

Morphology studies for the different samples were performed in a scanning electron microscopy. Fig. 4 shows SEM micrographs illustrating the morphology of the samples at different milling times, the microstructure of all samples was similar, being characterized by agglomerated grains; in all cases, aggregates size are of 1–5 μm and they are formed by small spherical particles of nanometric size, although it is difficult to distinguish the size of these particles due to the high density and compactness. The micrographics show that a significant decrease of the aggregates size takes place during the grinding of vanadium at the same time that an increase of the surface area occurs Table 1.

In order to compare the microstructure and the microhardness for the samples obtained by mechanosynthesis and thermal methods, two set of experiments were performed by SCRT: (a) samples 1–4, prepared at different reaction rates *C* at the same concentration of CO; these samples were prepared in a previ-

Table 3

Experimental conditions and characterization textural of final product obtained by SCRT method.

Sample	PCO (atm)	<i>C</i> (min <sup>-1</sup> )	<i>D</i> (nm)	S <sub>BET</sub> (m <sup>2</sup> /g)
1	0.0023	0.00027	64	5.8
2	0.0023	0.00060	68	3.7
3	0.0023	0.00100	72	1.5
4	0.0023	0.00200	73	1.7
5	0.0010	0.0016	80	1.9
6	0.0025	0.0018	48	1.8
7	0.0100	0.0014	50	2.3
8	0.0023	0.0010	57	27.2

ous work<sup>44</sup> in order to study the kinetic and mechanism of the carbothermal reduction of pentoxide of vanadium; and (b) samples 5–7, prepared at different concentrations of CO at the same reaction rate *C*. The experimental conditions and textural characterization of final products are shown in Table 3. On the other hand, sample 8 was obtained by carbothermal reduction of previously milled reactives (V<sub>2</sub>O<sub>5</sub> + 4C), in a planetary mill for 1 h. In this case, the reaction takes a lower temperature, as can be seen in Table 3. Furthermore the surface area is the highest, which is of great interest for catalyst uses. In all cases the final product was VN. The morphology studies for the different samples are shown in Fig. 5.

The micrographs for the samples obtained at the same partial pressure of CO but at different reaction rates, samples 1–4, show that when the reaction rates decrease, the particles and aggregate sizes also decrease. This behaviour is in good agreement with the measured values of surface area. Micrographs of samples 5–7 show that the samples prepared at the same reaction rate are formed by compact aggregate that increase their size as the partial pressure of CO increase. Sample 8 shows the lowest particle size and also the highest homogeneity.

Three of the samples obtained by mechanosynthesis, ground for 4, 6 and 8 h, respectively, and the samples prepared by the SCRT method were sintered in order to measure their microhardness. First, green bodies were obtained as pellets, with 400 mg of sample, by employing isostatic pressing. Then, they were sintered at 1750 °C during 1 h under helium atmosphere. The morphology studies for the different samples are shown in Figs. 4 and 5. The microhardness values were obtained using the equipment described in Section 2 (Table 4). The values of microhardness corresponding to the samples obtained by mechanosynthesis are in good agreement with those reported

Table 4

Densification and microhardness of sintered samples of VN.

Sample	Method of synthesis	Densification (%)	Microhardness (Hv)
4 h	Mechanosynthesis	98	1497
6 h	Mechanosynthesis	99	1462
8 h	Mechanosynthesis	100	1513
1	SCRT	81	901
4	SCRT	80	962
5	SCRT	93	1217
7	SCRT	92	957
11	Milling/SCRT	88	1423

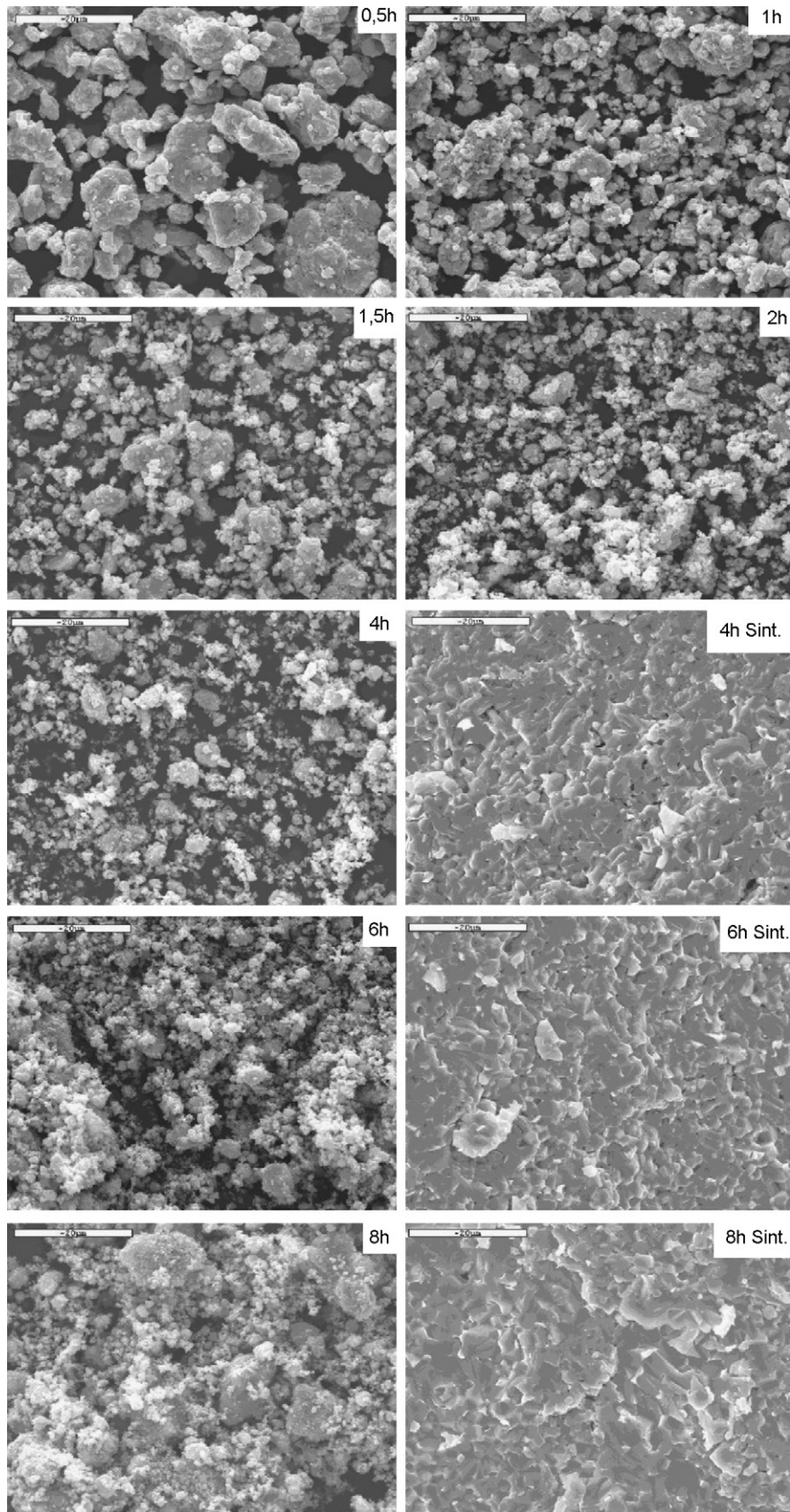


Fig. 4. Micrographs of vanadium ground under nitrogen atmosphere at 0.5–8 h, respectively, before and after sintering.

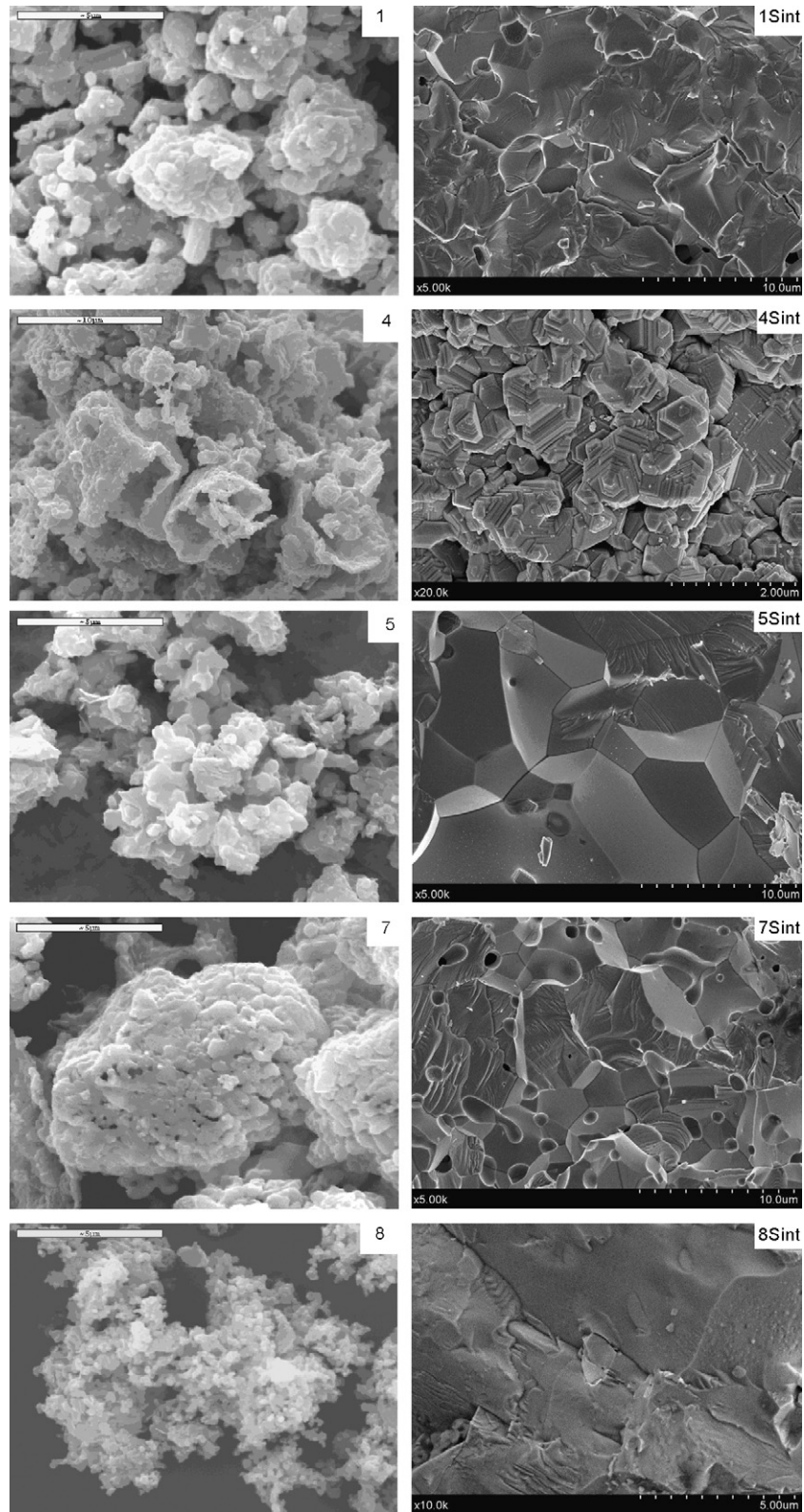


Fig. 5. Micrographs of VN samples obtained by SCRT method, before and after sintering.

in the literature<sup>18,45–48</sup> for these materials. On the contrary, the samples obtained from the SCRT method showed lower values of densification and microhardness. This result can be understood, if one considers, the microstructure of the unsintered

different samples (see Fig. 5). Only, sample 5, that shows a high homogeneity, has a high microhardness. It is interesting to point out that when there is a milling pre-treatment before employing the SCRT method, the properties of the obtained sample are

similar to those obtained from mechanosynthesis. The reaction temperature significantly decreases as a consequence of the precursor grinding when compared with the sample obtained under identical experimental conditions from the same unground precursor. This is why the surface area, densification and microhardness are the highest in this sample (Tables 3 and 4). The highest reactivity of the ground samples might be connected with the formation of prereacted nuclei that influence the morphology of the final product. The microstructure of the sintered samples (Fig. 5) is in good agreements with the above results. On the other hand, we can see in Fig. 4, showing the picture obtained from the samples ground from 4 to 8 h, that the densification increases with the grinding time. The high densification observed suggests that the microstructure developed in the ground powder promotes the cold welding of the particles showing compactness close to full density for the samples ground for 4–8 h.

In summary, we can conclude that the reactive milling is a good method to obtain this kind of compounds: the procedure is inexpensive, is made at room temperature, need short times of synthesis and nanometric particle sizes are obtained with a high sinterability and a very high microhardness. This procedure is a quite good method for both the synthesis and of the pre-treatment of samples before employing a thermal method.

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